



# Active and Durable PGM-free Cathodic Electrocatalysts for Fuel Cell Application

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**April 29, 2019**

**Project ID # FC305**

# Overview

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## Timeline

- Project Start Date: 01/01/19
- Project End Date: 12/31/20

## Budget

- FY19 DOE Planned:  
\$486,536
- Total DOE Funds  
Received to Date:  
\$28,310.88

## Barriers

- Activity of PGM-free ORR catalysts should be increased
- Decrease a cost of PGM-free catalysts manufacturing
- Increase the durability PGM-free catalysts

## Partners

- IRD Fuel Cells, Madeleine Odgaard
- University of Hawaii, Hawaii Natural Energy Institute (HNEI), Dr. Tatyana Reshetenko

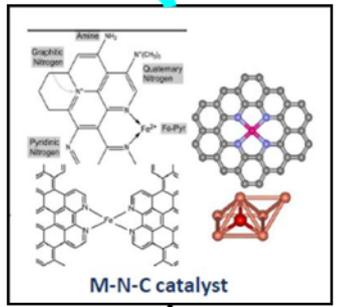
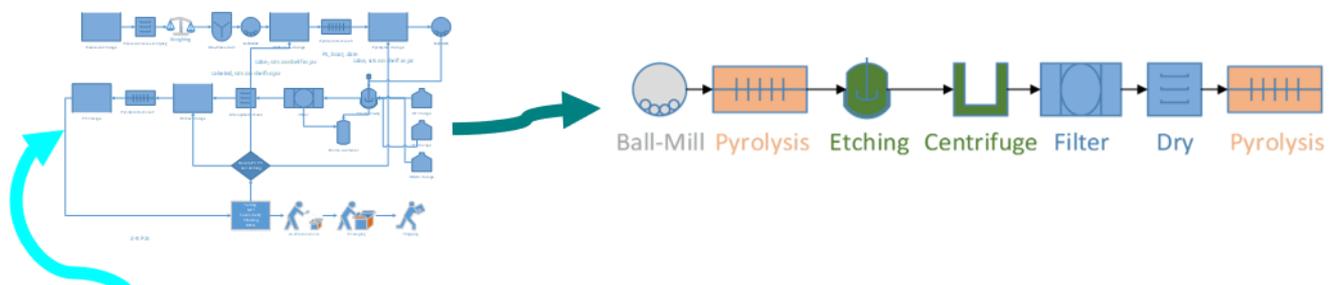
# Relevance: Objectives and Targets

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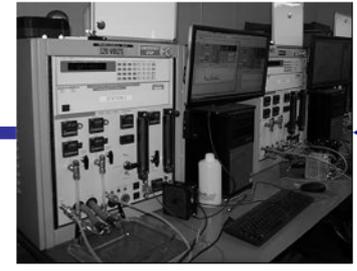
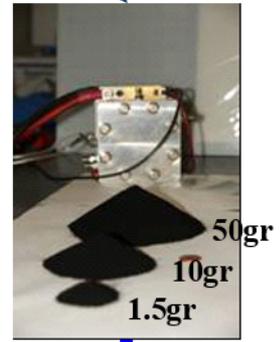


- Objectives: Development of PGM-free electrocatalysts for ORR; the catalysts will be scaled up to 50g batches (PP); PGM-free catalysts will be integrated into the industrial state-of-the-art MEAs (EWII) and comprehensively evaluated by electrochemical methods (HNEI).
- Relevance to DOE Mission: Inexpensive, highly active and stable PGM-free ORR catalysts commercially manufactured by US catalyst company will demonstrate required by DOE performance level due to understanding the electrochemical processes relevant to **PGM-free** materials in mass-produced MEAs.
- Targets
  - Demonstrate 0.044 A/cm<sup>2</sup> at 0.9V (iR-free, H<sub>2</sub>/O<sub>2</sub> configuration, 1bar O<sub>2</sub>, 80°C, 100%RH)

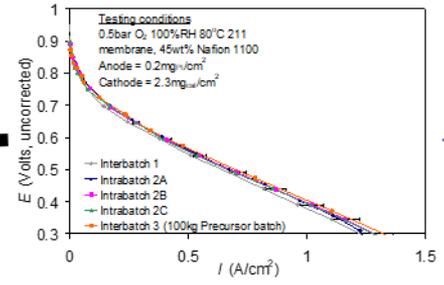
# Approach: Catalysts and Method



*Pajarito Powder is able to manufacture up to 200g of PGM-free ORR catalysts per batch*



US20080312073A1, WO2012174335A2, WO2013116754A1, WO2012174344A2, WO2014062639A1, WO2014011831A1, WO2014085563A1, WO2014113525A1,

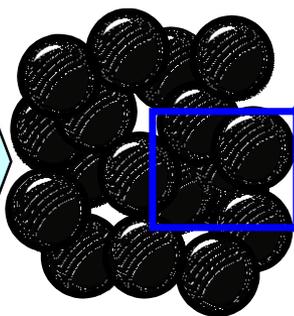


# Approach: VariPore™ Method

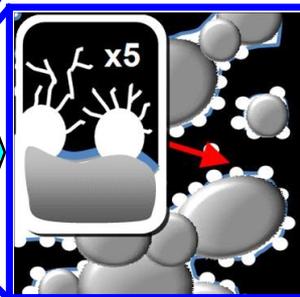
## Pore structure evolution



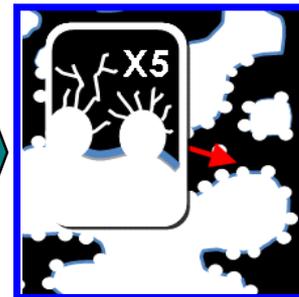
**Silica**  
Infused with  
precursors



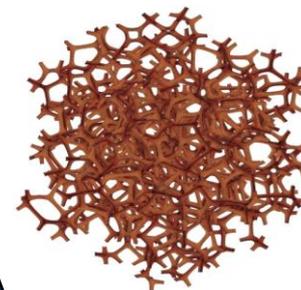
**Pyrolyzed**  
infused  
silica



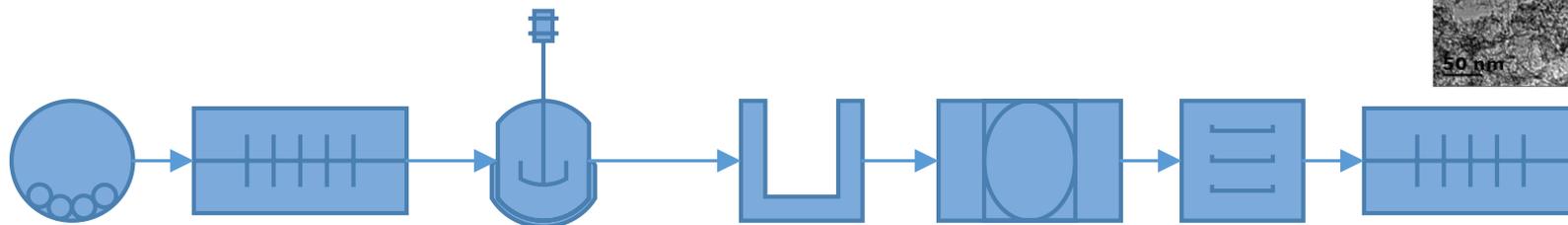
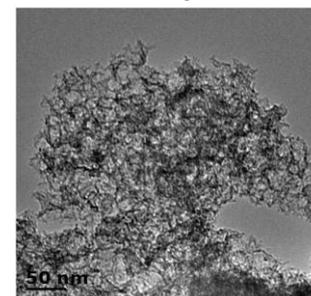
**Pyrolyzed**  
pore  
structure



**Etched**  
pore  
structure



**Porous**  
non-PGM  
catalyst



Ball-Mill Pyrolysis

Etching

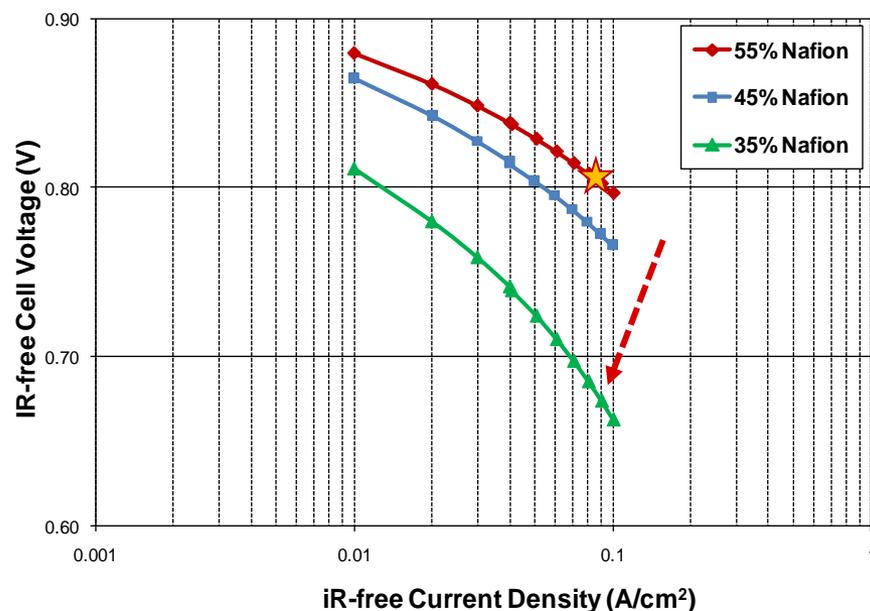
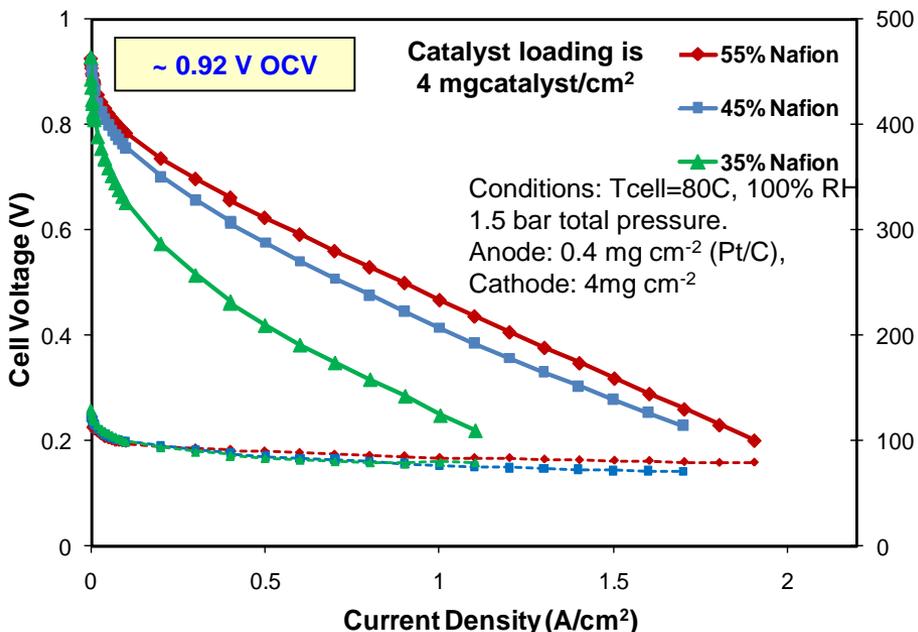
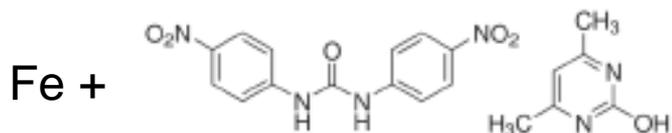
Centrifuge

Filter

Dry

Pyrolysis

# Approach: Preliminary Data



DOE EERE Project ID# FC086 AMR 2013 report, NTCNA testing

**Met DOE target (2013) of 100 mA/cm<sup>2</sup> at 0.8ViR-free in Oxygen**

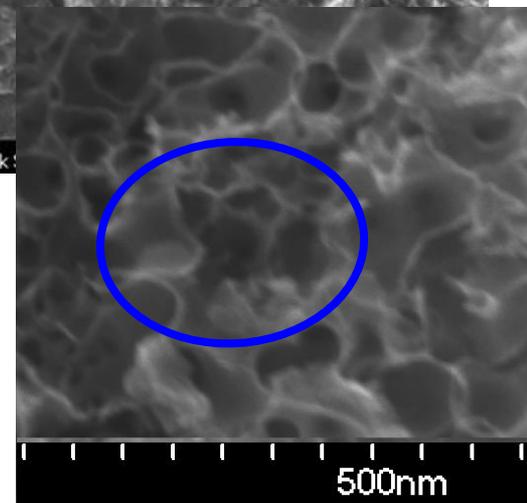
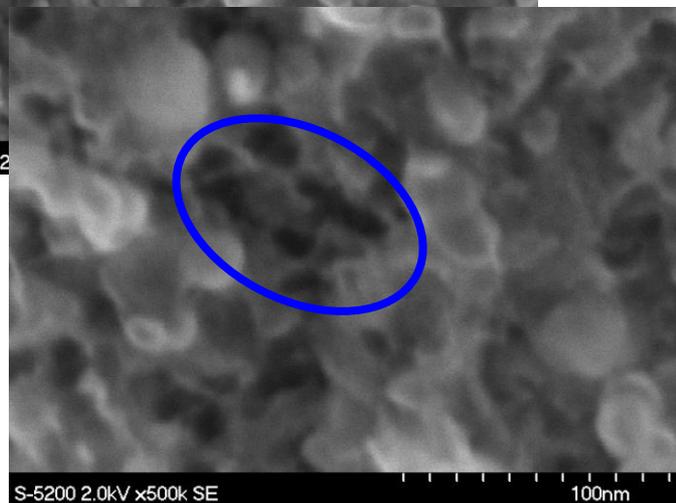
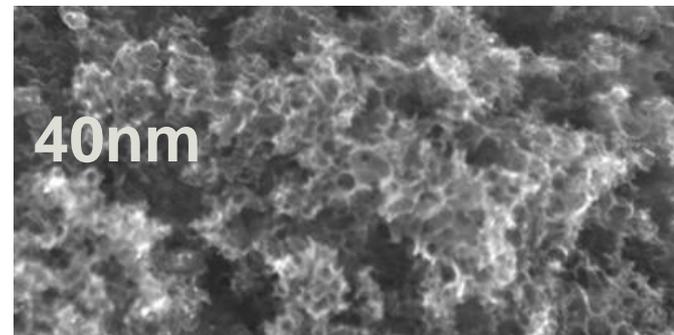
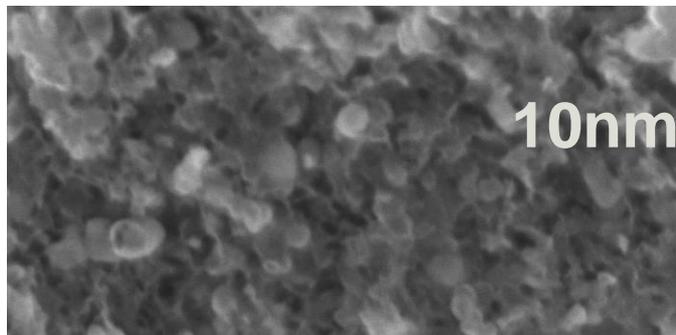
# Approach: Timeline and Milestones



## Milestone Summary Table

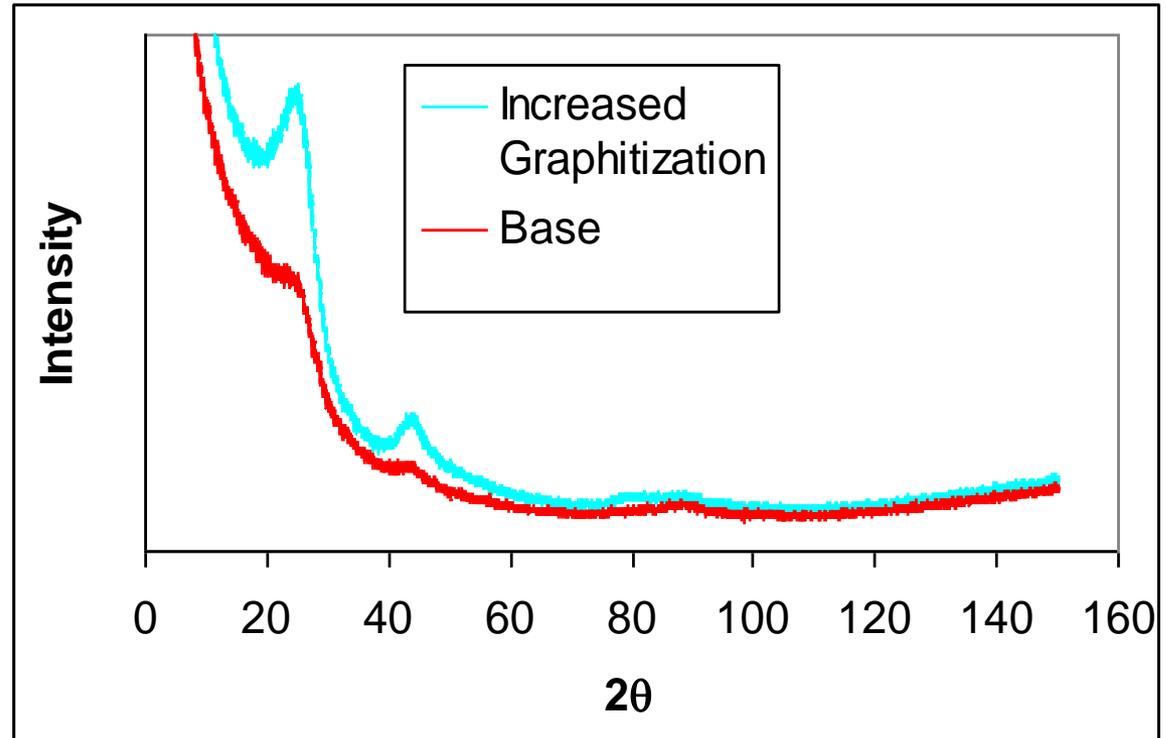
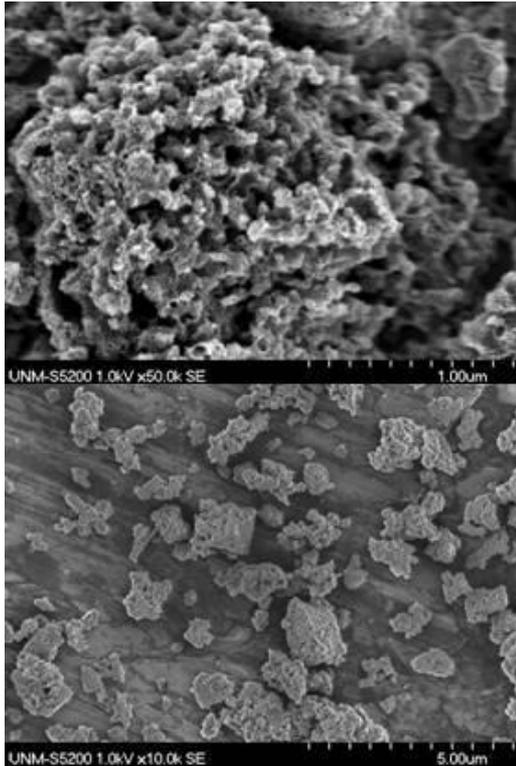
Recipient Name:		Alexey Serov, Pajarito Powder						
Project Title:		Active and Durable PGM-free Cathodic Electrocatalysts for Fuel Cell Application						
Task Number	Task or Subtask Title	Milestone Type	Milestone Number*	Milestone Description	Milestone Verification Process	Anticipated Date	Anticipated Quarter	Budget Period
<b>1. Benchmark performance of PGM-free catalysts in fuel cell tests</b>								
1.1	Stock Catalyst Characterization	Milestone	1.1	Correlation between synthesis parameters and morphology and chemistry of catalyst	Library of correlation. 15g of catalyst to EWII	1	1	1
1.2	Stock Catalyst integration in MEA	Milestone	1.2	Deliver 10 MEAs with stock catalyst	10 MEAs to HNEI and PP	2	1	1
1.3	Fuel Cell evaluation	Milestone	1.3	Activity will be compared with preliminary data obtained at Pajarito Powder: 0.025 A/cm <sup>2</sup> at 0.83V (iR-free), with H <sub>2</sub> /O <sub>2</sub> at 1.0 bar O <sub>2</sub> , 100%RH, 80 °C	Fuel cell tests at HNEI to confirm activity and establish benchmark	3	1	1
<b>2. Produce Gen-2 catalysts with atomically structured M-Nx active centers, integration into MEA and evaluation in fuel cell test</b>								
2.1	Catalyst Activity Improvement	Milestone	2.1	Deliver Gen-2 catalysts	15 g to EWII	6	2	1
2.2	Gen-2 MEAs	Milestone	2.2	Deliver 10 MEAs with Gen-2 catalyst Activity Target: MEA that produces 0.025 A/cm <sup>2</sup> at 0.85 V (iR-free), with H <sub>2</sub> /O <sub>2</sub> at 1.0 bar O <sub>2</sub> , 100%RH, 80 °C	Electrochemical fuel cell tests at PP, EWII and HNEI	9	3	1
2.3	Fuel Cell Tests: Active site Probing	Milestone	2.3	Recommendation to improve catalyst	Electrochemical analysis to EWII and PP	12	4	1
		Go/No-Go Decision	Go/No-Go #1	≥5cm <sup>2</sup> MEA that produces 0.025 A/cm <sup>2</sup> at 0.90 V (iR-free), with H <sub>2</sub> /O <sub>2</sub> at 1.0 bar O <sub>2</sub> , 100%RH, 80 °C	Measured/verified at HNEI and EWII	12	4	
<b>3. Improved morphology of PGM-free catalysts, Generation-3 of MEAs, mass transfer fuel cell evaluation</b>								
3.1	Bi-metallic catalysts	Milestone	3.1	Deliver Gen-2a catalysts (Activity Target in 3.3)	15 g to EWII	15	5/7	2
3.2	Catalyst Morphology Improvement	Milestone	3.2	Deliver Gen-3 catalysts (Activity Target in 3.3)	15 g to EWII	15	5/7	2
3.3	Gen-3 MEAs	Milestone	3.3	Deliver MEAs with Gen-3 catalyst. Activity target: 0.044 A/cm <sup>2</sup> at 0.85 V	10 MEAs to PP/ElectroCat	19	7/8	2

# Approach and progress: Pore Size Control



Design of M-N-C by VariPore<sup>®</sup> approach allows control catalyst morphology

# Approach and progress: Graphitization



Higher graphitization leads to more corrosion resistance under Start-Stop AST protocol

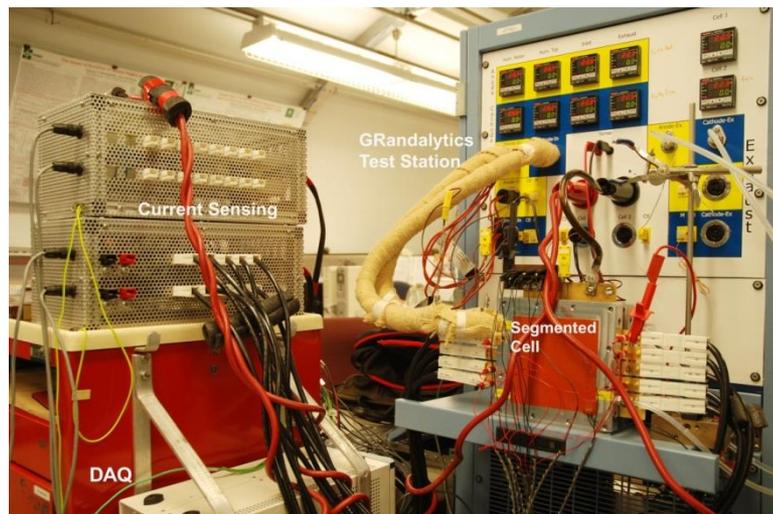
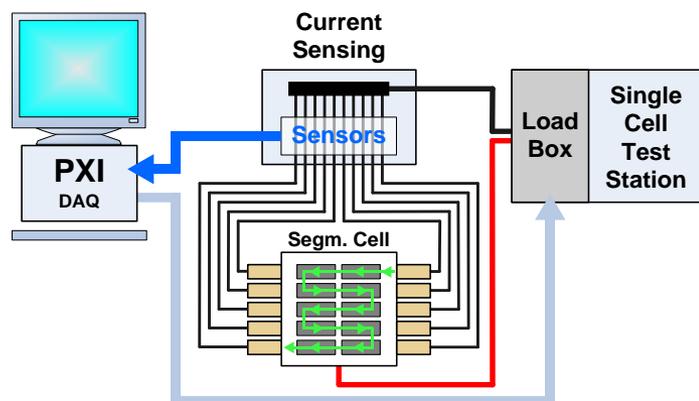
# Approach: Electrochemical characterization



## Subtask 1.3. Electrochemical characterization of the MEAs, standardization of activation procedure and testing protocols.

Application available characterization techniques (IV, EIS, CV)  
Use single cell (25, 50 cm<sup>2</sup>) and segmented cell (76 cm<sup>2</sup>) systems

### Segmented cell system



### High current mode ( $I < 2 \text{ A cm}^{-2}$ )

- VI curve, EIS

### Low current mode ( $I < 400 \text{ mA cm}^{-2}$ )

- Cyclic voltammetry
- Linear sweep voltammetry

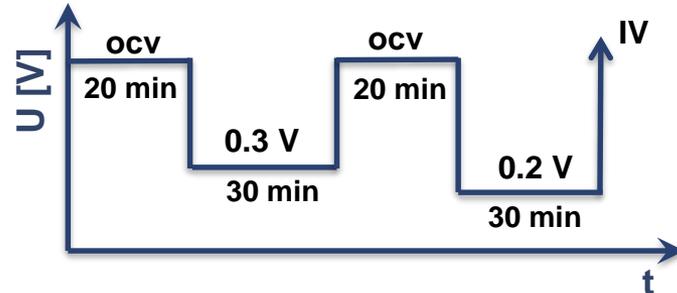
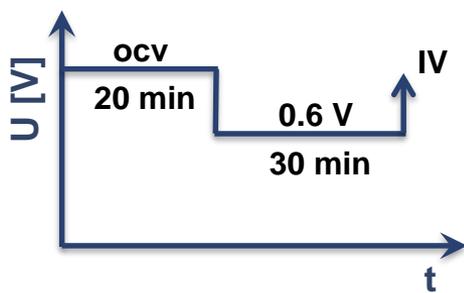
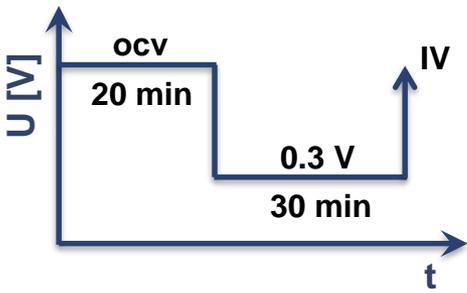
### The main advantages:

- operation of the system as a single cell,
- the use of standard testing procedures.

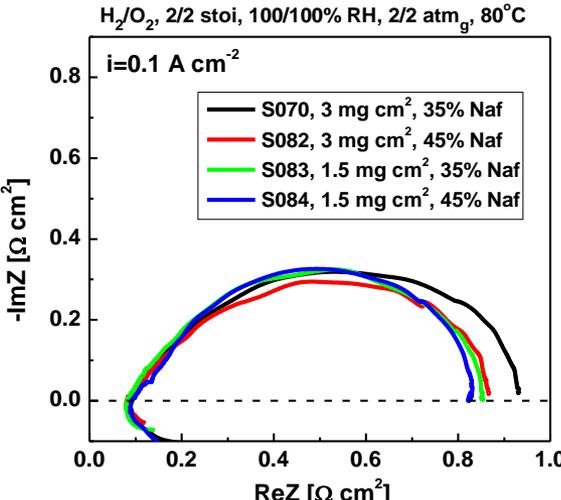
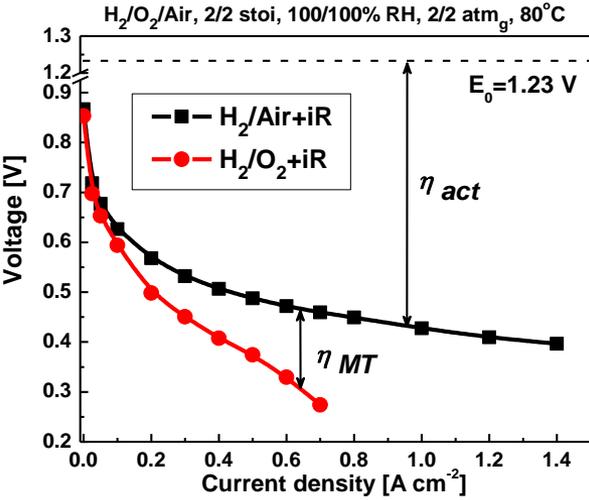
# Approach: Electrochemical characterization



**1. Activation protocols:** Testing several promising protocols chosen from previous experience (constant voltage hold at different voltage and duration):



## 2. Characterization: IV ( $O_2$ /Air), EIS, EIS modeling



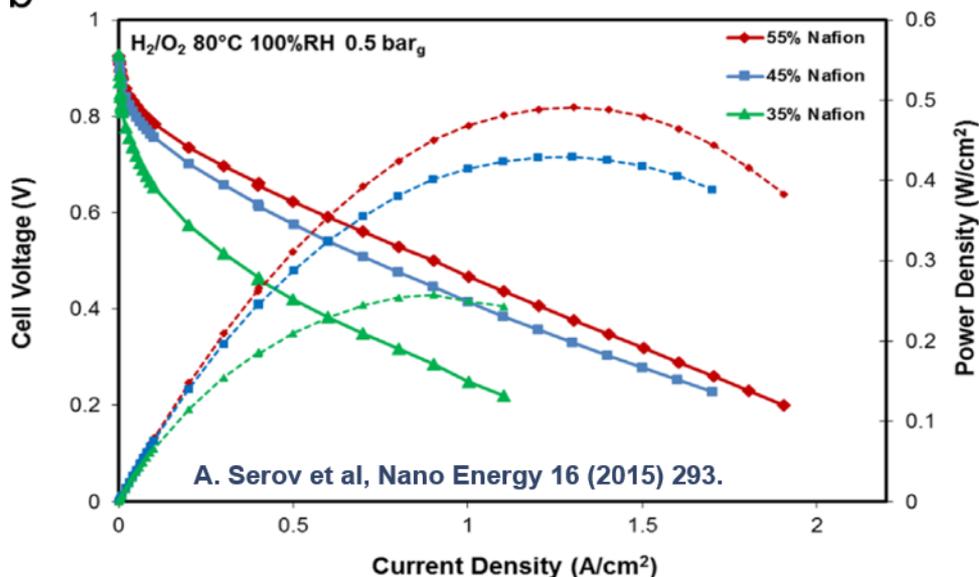
EIS model is based on a physical representation of the processes in MEA and provides the transport ( $O_2$  and  $H^+$ ) and kinetic parameters (Tafel slope) from the impedance spectra at relevant conditions.

# Approach: Electrochemical characterization

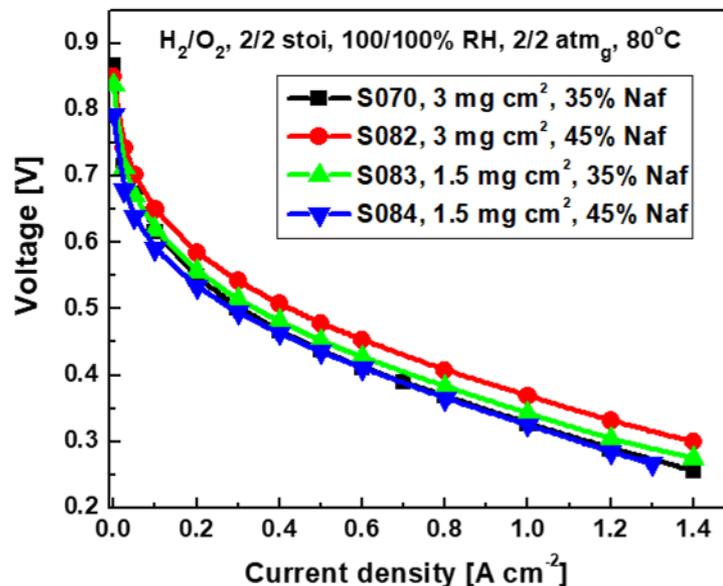


## 3. Testing protocols: Galvanostatic vs Potentiostatic control of load at IV measurements

**Potentiostatic mode, 5 cm<sup>2</sup> MEA**



**Galvanostatic mode, 76 cm<sup>2</sup> MEA**



IV measured under potentiostatic control of load has higher performance compared to galvanostatic IV. Catalyst degradation is facilitated by operation under galvanostatic conditions. It is important to recommend a standard testing protocol for obtaining reliable performance data and for comparison of the data between different teams.

# Approach: Active sites in PGM-free catalysts



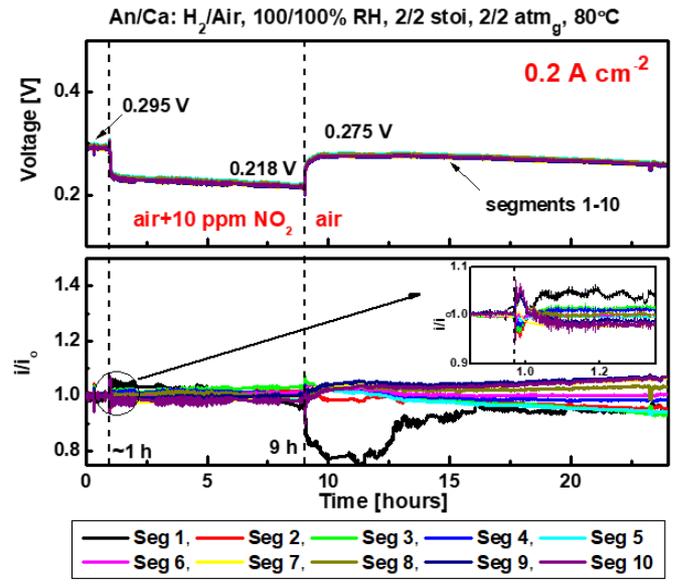
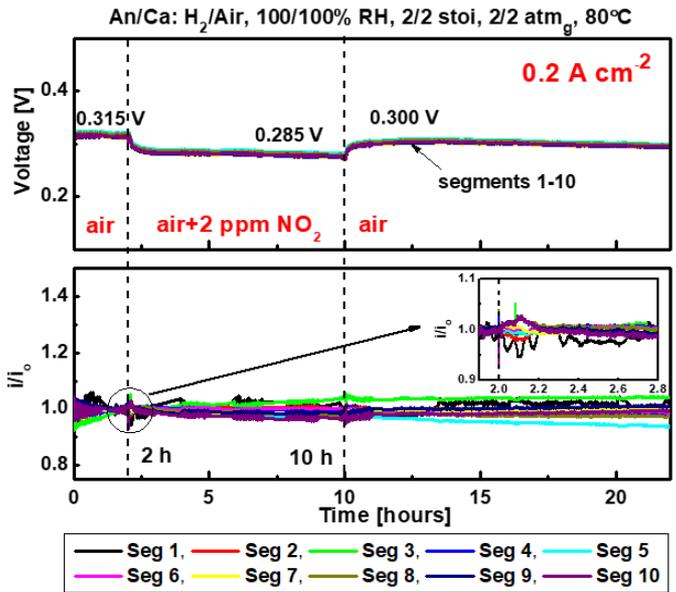
## Subtask 2.3. In situ quantification of active sites in PGM-free FCs.

Under this subtask we propose to investigate several relevant molecular probes which strongly interact with the M-N-C: NO, NO<sub>2</sub>, CH<sub>3</sub>CN, HSCN, H<sub>2</sub>S.

- 1) Select several potential probes and perform initial screening of their impact on PGM-free.
- 2) Assessment of the self-recovery of the PEMFCs.

### Preliminary data

T. Reshtenko et al, J Power Sources 324 (2016) 556.



**NO<sub>2</sub> and NO can substitute O<sub>2</sub> and poison Fe-N-C sites, resulting in performance loss. Thus, NO and NO<sub>2</sub> might be used as probe molecules to study Fe-N-C active centers.**

# Approach: Analysis of gas transport



## Subtask 3.3. Analysis of gas transport in PGM-free electrode structure.

To address mass transport limitations imposed by high catalyst loadings and thickness, different morphologies of PGM-free electrode structure will be evaluated by two approaches:

- 1) Deconvoluting voltage losses based on analysis of polarization curves measured with air, O<sub>2</sub> and He/O<sub>2</sub>;
- 2) Determining oxygen mass transport parameters using a novel method developed at HNEI. The method is based on a limiting current density distribution and application of diluents with varying molecular weights.

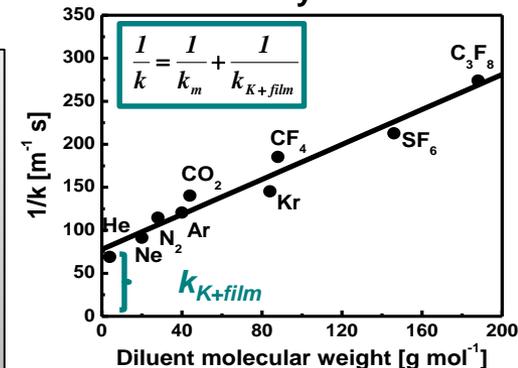
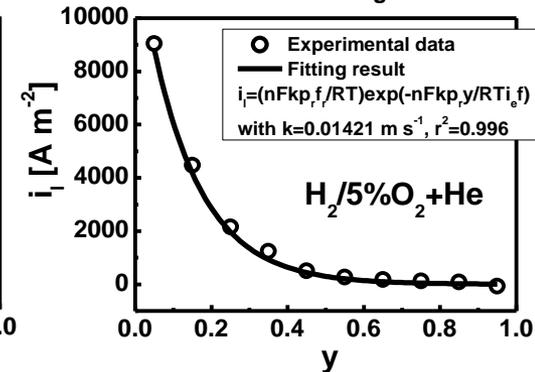
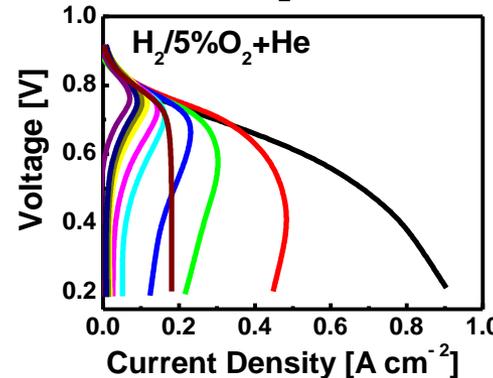
### Local limiting current density

$$i_{lim}(\tilde{y}) = \frac{nFk p_r \alpha_{O_2}^0}{RT} e^{-nFk p_r \tilde{y} / RT i_e f}$$

- $k$  - Mass transfer coefficient [m s<sup>-1</sup>]
- $y$  - dimensionless position along the flow field
- $p_r$  - dry inlet reactant stream pressure [Pa]
- $i_e$  - current density equivalent to inlet O<sub>2</sub> flow rate [A m<sup>-2</sup>]
- $f$  - inert gas to O<sub>2</sub> fraction in the dry inlet stream

The overall O<sub>2</sub> mass transfer coefficient ( $k$ ) is a series combination of molecular diffusion in the gas ( $k_m$ ) and Knudsen diffusion and diffusion through water/ionomer ( $k_{K+film}$ ). Different gas diluents affect only O<sub>2</sub> diffusion in gas phase ( $k_m$ ).  $k_{K+film}$  and  $k_m$  can be determined by extrapolation to zero diluent molecular weight.

An/Ca: H<sub>2</sub>/5%O<sub>2</sub>+He, 100/100% RH, 48.3/48.3 kPa<sub>g</sub>, 60°C



# Approach: Benchmark MEAs



**Subtask 1.1. Integration of Gen-1 catalyst into MEA structure, initial testing of catalyst, down select best performing catalyst and MEAs.**

**Application of electrode using EWII's standard coating technique**

## **1-Gen Catalyst layer integration:**

- Integration of PP stock (Gen-1) Fe-N-C catalyst into MEA for evaluation of benchmark performance.
- Establish effective material interfaces in MEAs
- Catalyst integrated into MEA using EWII standard method of catalyst layer design

**The main advantages:**

- Highly flexible innovative digital printing platform
- Enables rapid commercial prototyping and simple transition to high volume manufacturing.
- Aimed at all scales (from 25 cm<sup>2</sup> and up to industrial sizes ~5000 cm<sup>2</sup> )
- Apply to established Quality Control procedures

## **Process:**

- Uniform electrode coating and coat ability using EWII's industrial process routes
- Along with extremely uniform electrodes, complex electrode structures can be produced such as; spatial gradients of catalyst, ionomer and additives in all three dimensions, inter-digitated layer structures with any of the raw materials, and/or electrode patterning.



**1. Catalyst layer structure:** Input from sub-task 1.1 catalyst composition, surface area, particle size, pore size distribution and support characteristics to build 1-Gen structures:

- Apply standard PFSA (Nafion) and pre-screen BoL performance
- Selection of a standard ionomer concentration
- Make a set of 10 catalyst coated membrane (CCM) MEAs (25cm<sup>2</sup>) with a PGM-free catalyst loading on cathode of 3 mg cm<sup>-2</sup>

**2. Quality Control:** Apply and develop quality control on the final CCM/MEA including both in-line and off-line:

In-line:

- *Catalyst loading control*
- *Visual uniformity of electrode layers*
- *Data logging in coating equipment setup - controlled by accurate automated ink delivery system*
- *Automated vision control*

Off-line:

- *ROI Automated Optical Tool for measurement of critical dimensions*
- *Electrochemical performance test*
- *Visual inspection*
- *Thickness*



# Approach: Optimization of Gen-3 MEAs

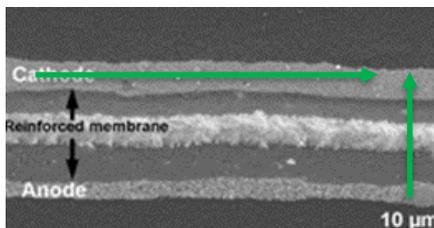


**Subtasks 2.2-3.2 Optimize and develop MEAs using PGM-free catalyst with improved morphology with focus on durability and water management**

**Optimization of catalyst layer and coating process techniques**

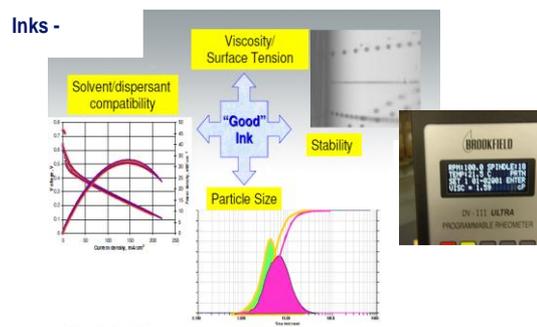
## Optimization of Gen-3 MEAs:

- Performance improvement by tailored electrode structures
- Fine tune catalyst-ionomer interaction: include all steps from Subtask 2.2: different solvent, additives and binders
- Emphasis will be dedicated to re-optimization of ionomer content, taking into account changed morphology of electrocatalyst.
- Adjust and develop coatings aimed for the new non-PGM catalyst system and investigate effect of spatial gradients and electrode patterning 2D (XY)

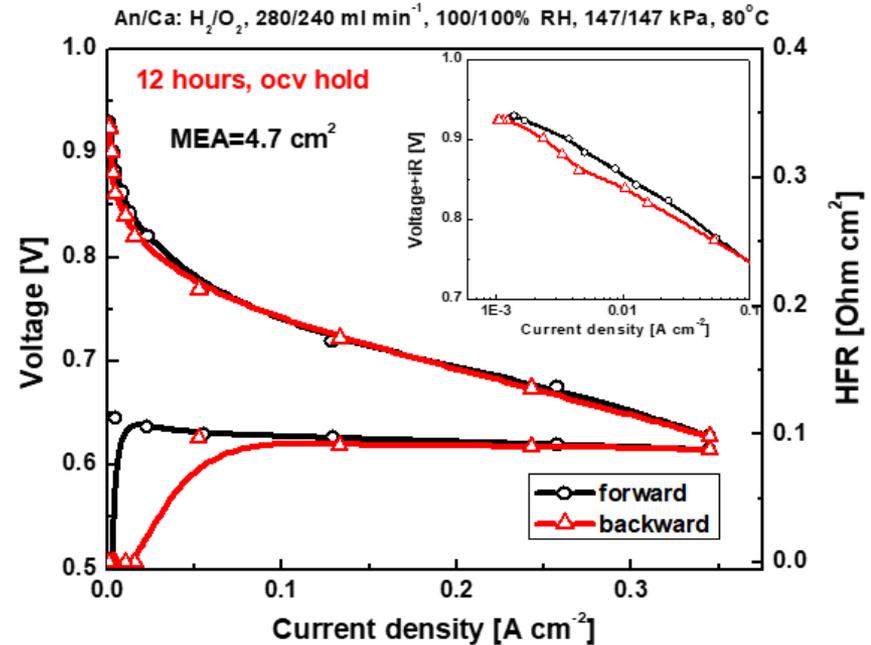
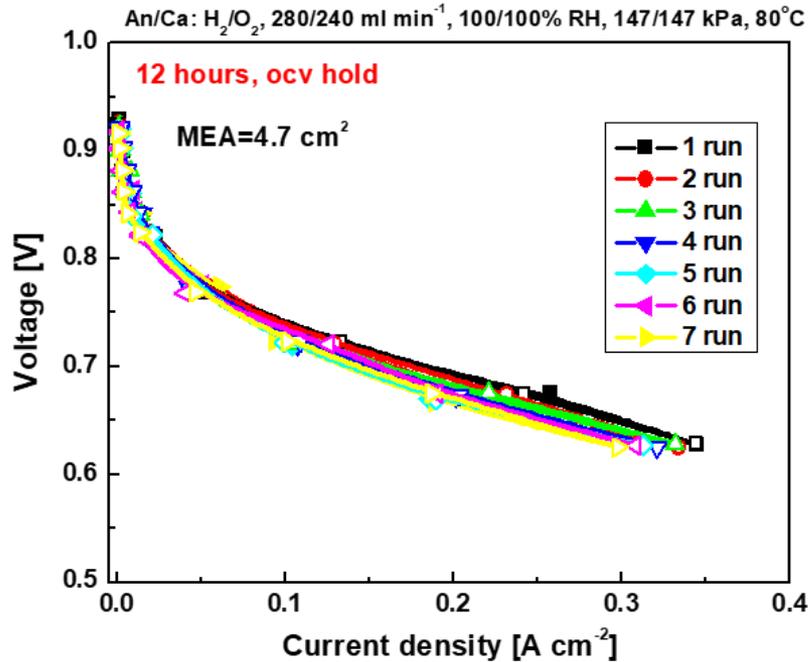


## Approach and Output:

- **Maximize catalyst utilization (ECSA)**
- **Reduce Mass transport limitations**
- **Enhance durability**
- **QC catalysts loading  $\pm$  % and catalyst layer thickness (5 points thickness measurements) should be in the 15% error bar range**

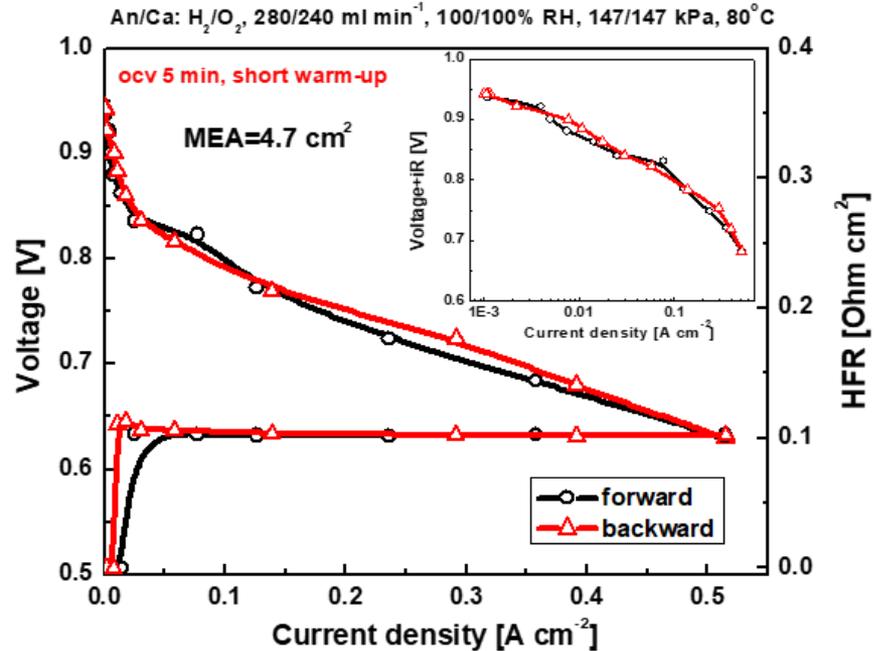
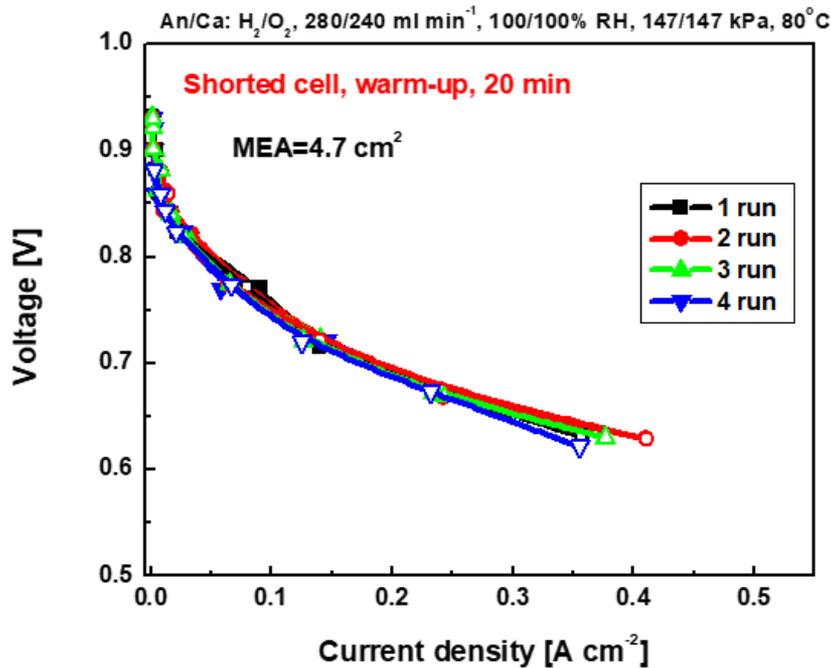


# Accomplishments and Progress



		1 IV run	2 IV run	3 IV run	4 IV run	5 IV run	6 IV run	7 IV run
fForward, iR corrected	U at 25 mA/cm <sup>2</sup> [V]	0.821	0.82	0.816	0.811	0.808	0.813	0.816
	U at 44 mA/cm <sup>2</sup> [V]	0.794	0.796	0.793	0.783	0.782	0.791	0.795
	I at 0.85 V [A/cm <sup>2</sup> ]	0.0115	0.0102	0.0094	0.0107	0.0087	0.0107	0.0109

# Accomplishments and Progress



		1 IV run	2 IV run	3 IV run	4 IV run
Forward, iR corrected	U at 25 mA/cm <sup>2</sup> [V]	0.829	0.836	0.83	0.825
	U at 44 mA/cm <sup>2</sup> [V]	0.813	0.815	0.805	0.8
	I at 0.85 V [A/cm <sup>2</sup> ]	0.014	0.0162	0.0129	0.0085

**Team achieved first milestone: 25 mA/cm<sup>2</sup> at 0.83V (Q1)**

# Collaborations

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- High Throughput synthesis and testing for improved catalysts
- High Throughput electrode optimization catalysts
- Advanced characterization of catalysts and electrodes before, during, and after testing
- Degradation and degradation mechanism analysis
- Benchmark catalysts for ElectroCat method development

# Remaining Challenges and Barriers

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- Project is in beginning, so majority of challenges and barriers are still to be solved
- Activation protocol is critically important and should be established and harmonized
- Decrease of performance from scan to scan can be a challenging task to overcome
- Higher initial activity of PGM-free catalysts should be achieved in order to maintain required performance after initial degradation

# Proposed Future Work

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- Provide a Generation 1 (Gen-1) of Pajarito's catalysts to IRD for integration into the industrial quality MEAs
- Evaluate the MEAs at HNEI under different activation protocols
- Pajarito: development of Gen-2 of PGM-free catalysts based on SOPO
- Based on the results obtained from IRD and HNEI re-formulate catalysts morphology and surface chemistry

# Summary

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- All contractual documents are executed and project officially started
- Pajarito Powder hosted an onsite kick-off meeting in December 2018
- Team started to work on the plan described in SOPO and first series of MEAs were fabricated by PP
- Series of MEAs with Gen-1 catalyst were provided to HNEI and under evaluation
- Preliminary data confirmed the importance of the activation protocol on overall catalyst performance
- Team successfully reached a first milestone (Q1) of 25 mA/cm<sup>2</sup> at 0.83V (MYRD&D recommended conditions)